Experimental evidence for high frequency transverse-like excitations in glasses

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Abstract

The dynamic structure factor of glassy and liquid glycerol has been measured by inelastic X-ray scattering in the exchanged momentum (Q) region Q=2÷23 nm^{-1} and in the temperature range 80÷570 K. Beside the propagating longitudinal excitations modes, at low temperature the spectra show a second non Q-dispersing peak at $\hbar\Omega_T \approx 8.5$ meV. We assign this peak to the transverse dynamics that, in topologically disordered systems, acquires a longitudinal symmetry component. This assignment is substantiated by the observation that, in the liquid, this peak vanishes when the structural relaxation time τ_α approaches Ω_T^{-1}, a behavior consistent with the condition $\tau_\alpha \Omega_T^{-1} >> 1$ required for the existence of a transverse-like dynamics in the liquid state.

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Understanding of the high frequency dynamics in the glassy state has recently progressed thanks to the development of the Inelastic X-rays Scattering (IXS) technique, allowing to measure the dynamics structure factor, $S(Q,\omega)$, in the mesoscopic momentum transfer, Q, range. This advance established the presence of longitudinal acoustic-like excitations [1] in topologically disordered systems. These excitations exist up to momentum transfer values close to the first maximum of the static structure factor, $S(Q)$, and have a characteristic Q-dependent broadening related to the topological disorder [2]. These results confirmed earlier predictions of many Molecular Dynamics (MD) and Normal Mode Analysis (NMA) simulation studies of disordered systems [3]. They are also consistent with a recent extension of the Mode Coupling Theory (MCT) to the glassy phase [4].

Despite these successes on the study of sound propagation at *THz* frequencies in topologically disordered systems, a satisfactory understanding of the high frequency *transverse* dynamics in glasses is still missing. Interestingly, beside the peaks associated with sound modes, theoretical and numerical works also predict a second excitation in the $S(Q,\omega)$ or in the related longitudinal current spectra [4–6]. This feature has been suggested to indicate the existence of a transverse-like dynamics in disordered systems, and it has been seen to survive also in the liquid state [6]. The main reason supporting the transverse-like nature of this second peak lies in the fact that it appears, at high Q's, in both the transverse and the longitudinal spectra, though being much more intense in the former ones. Other general characteristics of this second excitation are: *i)* It appears in the spectra at Q values larger than approximately one half the value of the first maximum of the $S(Q)$; *ii)* It shows a weakly Q-dispersing behavior; and *iii)* It has an "harmonic" origin, as pointed out by its presence in both MD and NMA simulations. In spite of these convincing numerical results, the firm experimental observation of this feature in glasses is still missing. It would be, therefore, of great interest to understand the behavior of this transverse dynamics in the glassy state, at the glass transition, and eventually, the conditions for its existence in the liquid state.

This Letter is dedicated to the experimental identification of this second excitation in

the high frequency dynamics of glycerol, an easily experimentally accessible prototype glass forming system. Using IXS, we report that in the glass, beside the sound modes, in the $S(Q,\omega)$ there is indeed a second excitation at $\hbar\Omega_T = E_T \simeq 8.5$ meV, showing up at exchanged momenta larger than 7 nm^{-1} with almost no Q dispersion. With increasing temperature this feature does not change energy, and progressively disappears in the tails of the central peak, becoming no longer observable above $\approx$500 K. At these high temperatures the width of the central peak of the $S(Q,\omega)$, consistently with the extrapolation of the temperature dependence of the viscosity, indicates that the structural relaxation time, τ_α, approaches the inverse frequency of the second peak. This observation suggests that this secondary peak (SP) does reflect the transverse dynamics. Indeed, the transverse dynamics is fully relaxed in the liquid at high temperatures, and appears as a vibrational contribution at low T, when the condition $\Omega_T \tau_\alpha(T) >> 1$ is fulfilled [7].

The experiment has been carried out at the very high resolution beam-lines ID16 and ID28 of the European Synchrotron Radiation Facility. The instruments consist of a backscattering monochromator and five independent analyzer systems, held one next to each other with a constant angular offset on a 7 m long analyzer arm. The utilized Si(11,11,11) configuration, with incident photon energy of 21748 keV, gives an instrumental energy resolution of 1.6 meV (FWHM) and an offset of 3 nm^{-1} between two neighbor analyzers. The momentum transfer is selected by rotating the analyzer arm. The energy scans at constant Q were performed by varying the monochromator temperature with respect to that of the analyzer crystals. For the low temperature measurements the glycerol sample, high purity anhydrous $C_3O_3H_8$, was put in a 20 mm long pyrex cylindrical cell closed by 1 mm thick diamond windows with a 4 mm opening. The cell was loaded inside an argon glove box and then placed in a closed cycle cryostat. The high temperatures measurements have been performed loading a 20 mm long nickel cylinder closed by two sapphire windows, (1 mm thick, 8 mm diameter) and heated in a standard oven operated in vacuum.

The IXS data collected on the glycerol glass sample at T=79 K are reported in Fig. 1. Beside an intense central line, the spectra show a Q dependent inelastic signal. In the low

Q region, this is characterized by a single feature whose energy position and width increase with Q. This excitation is due to the propagating longitudinal acoustic modes, as already established in previous works [8,2]. Thanks to the increased statistical accuracy with respect to previous experiments, in the present data, one observes also that at Q larger than 7 nm^{-1} a new weakly dispersing feature appears at ≈10 meV. This feature, the secondary peak shown in the right panel of Fig. 1, is particularly evident in the spectra at the highest reported Q values. The data have been fitted by the convolution of the experimental resolution function with a model function, weighted by the detailed balance, composed by: 1) a delta-function to account for the central line, 2) a Damped Harmonic Oscillator (DHO) for the longitudinal mode, and 3) a lorenzian for the SP, which is statistically relevant only in the spectra at $Q \gtrsim 6$ nm^{-1}. This model well represents the experimental data, as shown in Fig. 1.

In Fig. 2, we report the energy positions of the two features: the longitudinal acoustic mode (Ω_L) and the SP (Ω_T). The slope of Ω_L consistently reproduces, in the low-Q linear dispersion region, the correct value of the velocity of sound (v_L=3370±30 m/s). In the high Q region, we still observe a dispersion of Ω_L that, as expected, has a maximum at a Q-value approximately half way from the maximum of the $S(Q)$, and a minimum in the Q region where the $S(Q)$ has a maximum. This dispersion of Ω_L is consistent with the concept of pseudo Brillouin zone in disordered systems, as discussed elsewhere [9]. The SP is observed at the essentially Q-independent energy $\hbar\Omega_T$=8.5±0.5 meV. This feature, as can be directly evinced from a more detailed analysis of the data in Fig. 1, shows an interesting Q-dependence in its intensity, which increases with increasing Q. This may be due to various effects, among which the expected Q^2 dependence of the cross-section of a non dispersing mode (localized or internal molecular mode), and/or the possible Q-dependence of the longitudinal vs transverse symmetry components of the eigenvectors associated to this mode. It is obviously crucial to investigate these points to understand the origin of the SP. To this purpose we studied this feature as a function of temperature in order to investigate its evolution across the liquid-to glass transition ($T_g \approx 180$ K) and up to the normal liquid phase. This temperature dependence has been studied at Q=17 nm^{-1} from T=170 K (in

the glassy phase) to T=570 K. The Stokes side of the spectra at selected temperatures is reported in Fig. 3.

The Q value of 17 nm^{-1} has been chosen in order to neglect the contribution of the longitudinal mode, while having still the SP well pronounced in the glass. The fitting function consists of a delta function for the central line (replaced by a Cole-Davidson function for $T \gtrsim 400$ K, when the intrinsic broadening can be distinguished by the mere resolution linewidth), and a lorenzian function for the SP. Both spectral features show a striking T-dependence: increasing T the central line gets increasingly broader and the SP becomes hardly visible already at ≈350 K. As long as the SP is statistically significant one finds that its energy position and width are T-independent, while its intensity decreases. The fits to the data provide a quantitative description of these behaviors, and, as reported in the inset of Fig. 3, the ratio between the integrated intensities of the SP to the central peak sharply decreases at high temperatures. As shown in Fig. 4, this behavior is opposite to the increase that one would normally expect. Indeed: *i)* The central peak intensity should slightly decrease, following the Debye-Waller T dependence, and *ii)* The SP intensity should increase following the Bose-Einstein (BE) statistics.

To emphasize further the statistical significance of the SP intensity behavior, and to show that this feature is not simply lost in the tails of the increasingly broader central peak, we report at T=563 K the simulation (dot-dashed line) of how the spectrum should look like under the following assumptions: *i)* A central line with a constant integrated intensity (the same as the spectrum at $T = 170$ K) and the observed width, *ii)* A SP obtained from the glass spectrum at T=170 K, keeping constant the energy position and width, and increasing the integrated intensity according to the BE statistics. This simulation underlines the observed disappearance of the SP at high T beyond any statistical uncertainty. The temperature dependence of the SP allows us then to exclude on a general ground that this excitation is due to an internal molecular mode. Indeed, if this were the case, one should expect a behavior giving rise to the simulated spectrum in the upper panel of Fig. 3.

Finally, the broadening of the quasi-elastic line which appears in the high-temperature

spectra is quantified in Fig. 5, where we report the structural relaxation time as obtained from the Cole-Davidson contribution to the fitting function which we have used. These values are in good agreement with light scattering and viscosity data [10,11], testifying the reliability of the whole presented data analysis.

On the basis of the reported results, we propose that the SP is due to the transverse-like acoustic dynamics in a topologically disordered structure. In fact, in the glycerol glass two excitation branches are present, as shown in Fig. 2. This result is very similar to those obtained in MD simulations, where indeed these two excitations have been assigned, respectively, to the acoustic longitudinal-like and to the transverse-like dynamics on the basis of the analysis of calculated longitudinal and transverse current spectra. This assignment is also consistent with the observation that the SP intensity increases with increasing Q. Indeed, on decreasing the length scale, the local disorder forbids more and more the pure polarization of the eigenvectors, thus leading to the mixing of the longitudinal and transverse symmetries. Clearly, it is exactlty due to this mixing that the longitudinal part of the transverse-like excitation comes out in the $S(Q,\omega)$. This interpretation on the origin of the SP is additionally supported by the behavior observed in the liquid phase. Indeed, a vibrational transverse-like dynamics in the liquid state can only be supported when the structural relaxation time is much longer than the transverse vibration period (elastic limit), i. e. when the local structure is frozen for long enough time that a shear stress does not decay through relaxational processes. Conversely, in liquids at high temperature, where the condition $\Omega_T\tau_\alpha >> 1$ is no longer fulfilled, the vibrational transverse dynamics is no longer allowed and the SP disappears. It is important to point out that this behavior is distinctly different from that of the longitudinal acoustic excitations. In fact - as experimentally observed - these latter ones keep their vibrational nature independently of the value of $\Omega_L\tau_\alpha$, which only affects the value of the sound velocity and absorption.

In conclusion, we report experimental evidences of the existence of a transverse-like dynamics in glasses and liquids at THz frequencies. This dynamics gives rise to a well defined and *non* Q-dispersing excitation, consistently with MD simulations. We expect that

this feature is a general property of disordered matter, and that it should be universally observed. Indications in this direction come not only from MD simulations [6,12], but also from experimental data on glassy SiO_2 and liquid water [13,5]. Future work on the dynamics in disordered systems should consider the contribution of this high frequency transverse-like dynamics to the vibrational density of states. This could be particularly relevant in the case of glasses, due to the possible contribution and/or relation of this transverse-like dynamics to the well known low temperature anomalies.

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REFERENCES

[1] F. Sette, M. Krisch, C. Masciovecchio, G. Ruocco, and G. Monaco, Science **280**, 1550 (1998); O. Pilla, et al., Phys. Rev. Lett. **85**, 2136 (2000) and references therein.

[2] G. Ruocco, et al., Phys. Rev. Lett. **83**, 5583 (1999).

[3] S.N. Taraskin and S.R. Elliot, Europhys. Lett. **39**, 37 (1997), ibid. Phys. Rev. B **56**, 8605 (1997). M.C. Ribeiro, M. Wilson and P.A. Madden, J. Chem. Phys. **108**, 9027 (1998), ibid. J. Chem. Phys. **109**, 9859 (1998). R. Dell'Anna, G. Ruocco, M. Sampoli, and G. Viliani, Phys. Rev. Lett. **80**, 1236 (1998). J.L. Feldman, P.B. Allen and S.R. Bickham, Phys. Rev. B **59**, 3551 (1999). J. Horbach, W. Kob and K. Binder, Eur. Phys. J. B **19**, 531 (2001).

[4] W. Goetze, and M. R. Mayr, Phys. Rev. E **61**, 587 (2000).

[5] F. Sette, et al., Phys. Rev. Lett. **77**, 83 (1996).

[6] M. Sampoli, G. Ruocco, and F. Sette, Phys. Rev. Lett. **79**, 1678 (1997).

[7] J. P. Bonn, and S. Yip, *Molecular Hydrodynamics*, McGraw-Hill, New York, 1980.

[8] C. Masciovecchio, et al., Phys. Rev. Lett. **76**, 3356 (1996)

[9] T. Scopigno, M. D'Astuto, M. Krisch, G. Ruocco, F. Sette, Phys. Rev. B **64**, 012301 (2001).

[10] D.M. Paolucci, K.A. Nelson, J. Chem. Phys. **112**, 6725 (2000).

[11] H. Landolt, R. Bornestein sec. 25-1, vol. II/5a, VI edition.

[12] R. Dell'Anna, Ph.D. Thesis, L'Aquila (1997), unpublished.

[13] G. Ruocco, F. Sette, J. Phys. C **13**, 9141 (2001).

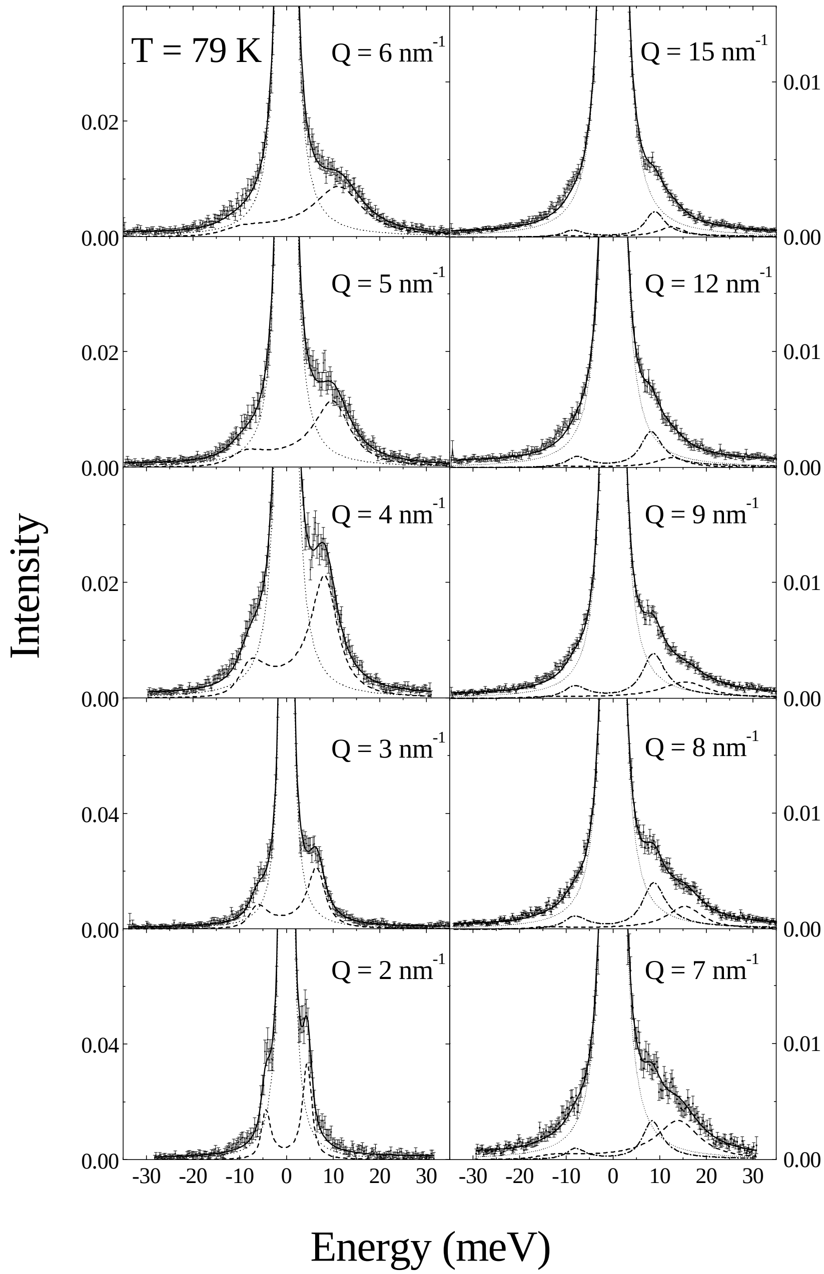

FIG. 1. IXS spectra of glassy glycerol at $T = 79$ K for selected values of the exchanged wavevector (dots with error bars). The total fitting result (full line) is also reported, along with the genuine inelastic signal relative to the longitudinal mode (dashed line). Above $Q \gtrsim 6$ nm^{-1} (right column) we included a SP with lorenzian shape in the fitting function (dotted-dashed line). The instrumental resolution is also shown (dotted line).

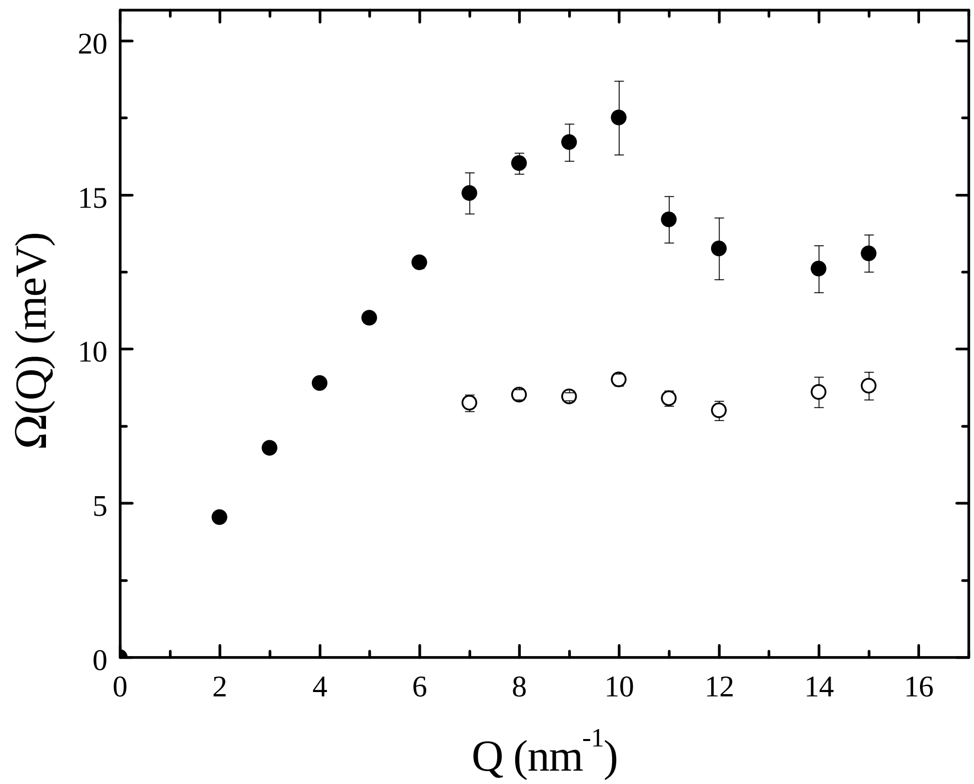

FIG. 2. Energy position of the longitudinal (full dots) and transverse (open dots) acoustic modes at $T = 79$ K, as determined by the fitting procedure described in the text.

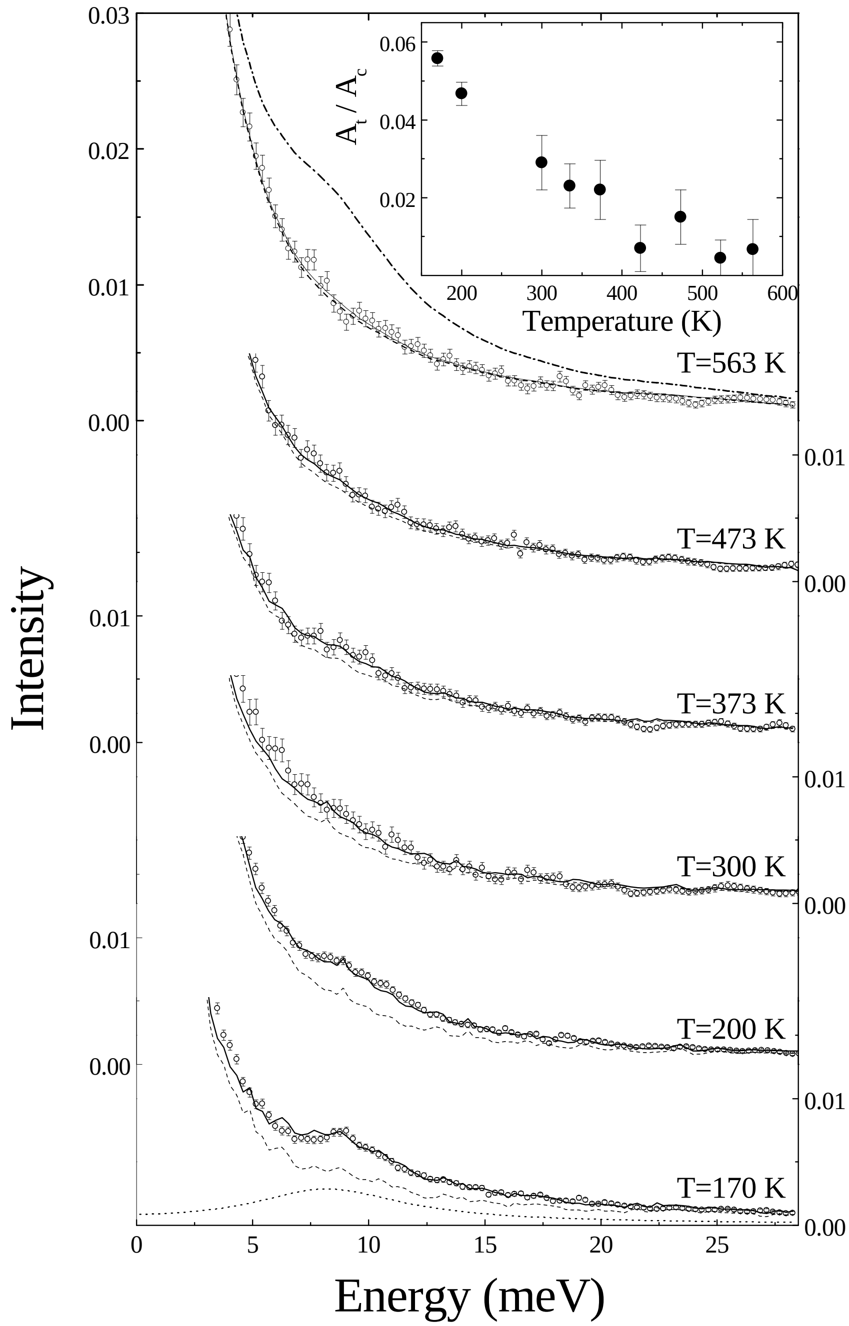

FIG. 3. Stokes side of the IXS spectra of glycerol at $Q = 17$ nm^{-1} at selected temperatures (open dots with error bars). Also reported are the best fits to the data (full line) and the central peak contribution (dashed line). For $T = 170$ K we also report the inelastic signal (at the other temperatures it simply scales for an amplitude factor), while at $T = 563$ K we show how the spectrum should appear if the SP were related to some intramolecular mode. In the inset we report the inelastic (SP mode) to elastic intensity ratio as determined by the fit.

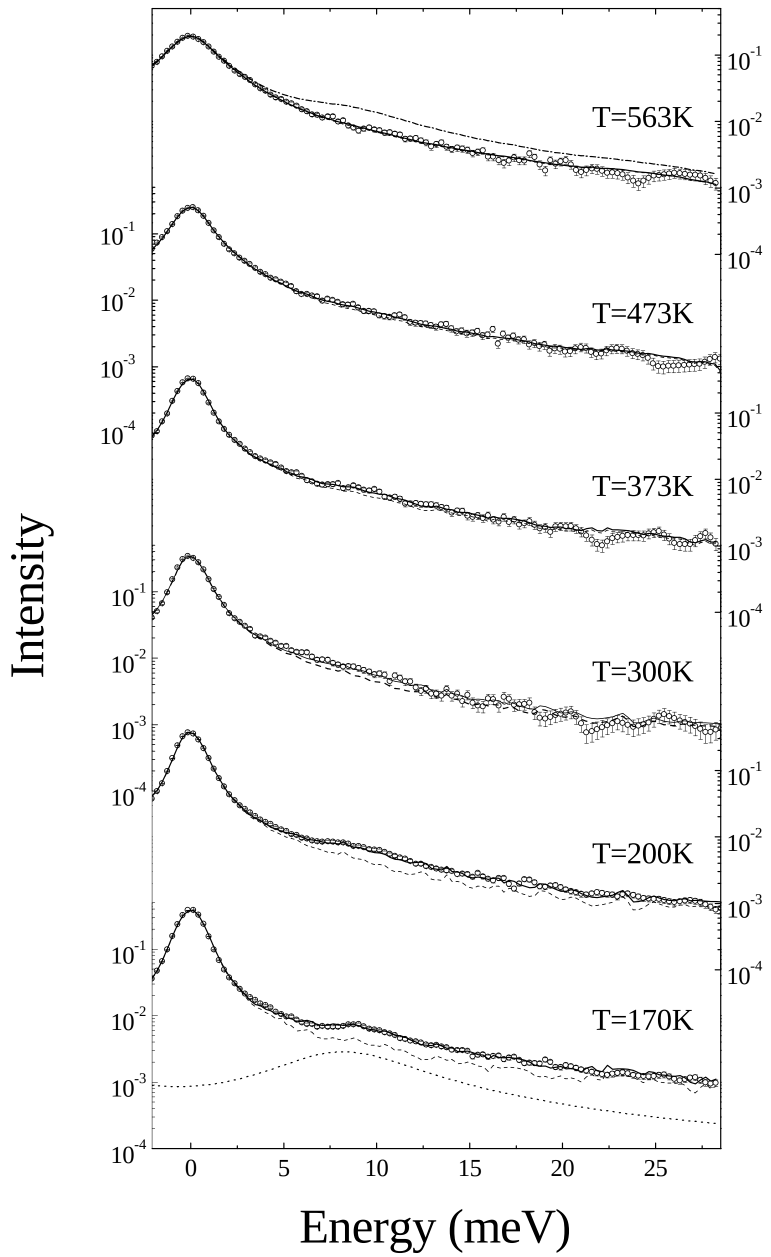

FIG. 4. Same as Fig. 3 but in logarithmic scale, to better emphasize the broadening of the central peak above T_g.

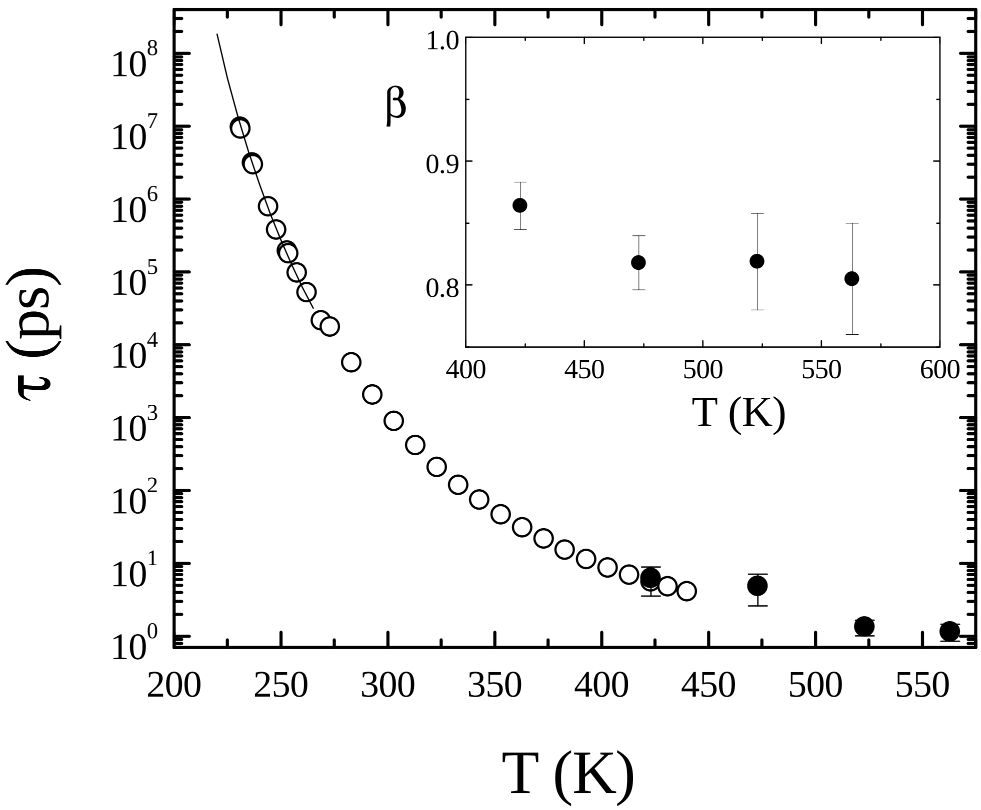

FIG. 5. Values of the structural relaxation time in glycerol as function of temperature. Full dots: this work, determined in the liquid at high temperature from the central peak broadening. Full line: light scattering. Open dots: viscosity data scaled by an arbitrary factor. Inset: values of the stretching exponent of the Cole-Davidson function used to describe the central peak at high temperature